

# The Optical absorption study of $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3$ : $\text{MnO}$ glass system

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**Abstract**— The structure of  $30 \text{ Li}_2\text{O} - (10-x) \text{ ZnO} - 60 \text{ B}_2\text{O}_3$ :  $x \text{ MnO}$  glass system with  $0 \leq x \leq 0.6 \text{ mol\%}$  was prepared. The optical absorption indicates that the presence of manganese ions predominantly in  $\text{Mn}^{2+}$  state occupy tetrahedral positions when the concentration of  $\text{MnO}$  at about  $0.4 \text{ mol\%}$ ; whereas beyond  $0.4 \text{ mol\%}$  the manganese ions seem to exist in  $\text{Mn}^{3+}$  state.

**Index Terms**—Glasses,  $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3$ , Manganese ions, Optical absorption spectra.

## 1. INTRODUCTION

Transition metal oxides constitute probably one of the most interesting classes of solids, exhibiting a variety of structures and properties. The nature of metal oxygen bonding can vary between nearly ionic to highly covalent or metallic. The unusual properties of transition metal oxides are clearly due to the unique nature of the outer d-electrons. The phenomenal range of electronic and magnetic properties exhibited by transition metal oxides is especially note worthy.

Transition metal oxides (TMOs) exhibit a rich collection of interesting and intriguing properties, which can be tailored for a wide variety of applications including low-loss power delivery, quantum computing using cooper pairs, ultra high-density magnetic data storage and more recently spintronic applications. Many transition metal oxides have been prepared in bulk form or as thin films, which paved the way for intensive research studies in the past several decades.

The transition metal ions such as manganese dissolved in  $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3$  glass matrix even in very small quantities make these glasses colored and have strong influence over the insulating character and optical transmission of these glasses. It may be useful to compare the environment of manganese ions in various other glass systems like silicates, fluorides, borate, arsenates etc., with that of the present glass system. For example, in some borate glasses when manganese oxide is present in low concentrations, the manganese ions are reported to be in tetrahedral positions whereas in high concentration range, the ions are observed to occupy octahedral positions [1]. The objective of the present investigation is to have a comprehensive understanding over the topology and valence states of manganese ions (when present in small quantities) in  $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3$  glass network, by a systematic study of optical absorption spectra.

## 2. Experimental Work

Within the glass-forming region of  $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3$  glass system, the following particular compositions with

successive increase in the concentration of  $\text{MnO}$  are chosen for the present study:

$M_0$ :  $30 \text{ Li}_2\text{O} - 10 \text{ ZnO} - 60 \text{ B}_2\text{O}_3$  (pure)  
 $M_1$ :  $30 \text{ Li}_2\text{O} - 9.9 \text{ ZnO} - 60 \text{ B}_2\text{O}_3$ :  $0.1 \text{ MnO}$   
 $M_2$ :  $30 \text{ Li}_2\text{O} - 9.8 \text{ ZnO} - 60 \text{ B}_2\text{O}_3$ :  $0.2 \text{ MnO}$   
 $M_3$ :  $30 \text{ Li}_2\text{O} - 9.7 \text{ ZnO} - 60 \text{ B}_2\text{O}_3$ :  $0.3 \text{ MnO}$   
 $M_4$ :  $30 \text{ Li}_2\text{O} - 9.6 \text{ ZnO} - 60 \text{ B}_2\text{O}_3$ :  $0.4 \text{ MnO}$   
 $M_5$ :  $30 \text{ Li}_2\text{O} - 9.5 \text{ ZnO} - 60 \text{ B}_2\text{O}_3$ :  $0.5 \text{ MnO}$   
 $M_6$ :  $30 \text{ Li}_2\text{O} - 9.4 \text{ ZnO} - 60 \text{ B}_2\text{O}_3$ :  $0.6 \text{ MnO}$

The glasses used for the present study are prepared by the melting and quenching techniques [2-4]. . Batch materials to produce  $10 \text{ g}$  of each glass were accurately weighed, thoroughly mixed in an agate mortar and melted in a platinum crucible. Appropriate amounts (all in  $\text{mol\%}$ ) of reagent grades of  $\text{H}_3\text{BO}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{ZnO}$  and  $\text{MnO}$  powders were thoroughly mixed in an agate mortar and melted in a thick walled platinum crucible in the temperature range  $1000-1050^\circ\text{C}$ . The furnace used was a PID temperature controlled furnace. The glasses were melted in a thick walled platinum crucible for an hour till a bubble free liquid was formed. The resultant melt was poured on a rectangular brass mould (having smooth polished inner surface) held at room temperature and subsequently annealed at  $200^\circ\text{C}$  in another furnace. The glasses were then ground and optically polished. The approximate final dimensions of the glasses used for present study are  $1 \text{ cm} \times 1 \text{ cm} \times 0.2 \text{ cm}$ . The optical absorption spectra of the glasses were recorded using a JASCO Model V-670 Spectrophotometer in the wavelength range  $300-2200 \text{ nm}$ .

## 3. Results and Discussion

Fig. 1 a shows, the optical absorption spectra of  $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3$ :  $\text{MnO}$  glasses in the wavelength region of  $350-600 \text{ nm}$ . The absorption edge appeared at  $420 \text{ nm}$  for pure glass  $M_0$  is shifted slightly to a lower wavelength with increase in the concentration of  $\text{MnO}$  (up to  $0.4 \text{ \%}$ ) and beyond this concentration, the edge is shifted towards slightly higher wavelength. The spectrum of the glass  $M_1$  (Fig.1a) has exhibited two absorption bands: i) a broad band at  $520 \text{ nm}$  and ii) another band at  $415 \text{ nm}$  respectively corresponding to the transitions  ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{1g}(\text{G})$  and  ${}^6\text{A}_1(\text{S}) \rightarrow {}^4\text{T}_2(\text{G})$  of  $\text{Mn}^{2+}$  ions. To be more precise, the first band is identified due to the octahedral transition where as the second one is due to the tetrahedral transition of divalent manganese ion [5-7]. With increase in the concentration of  $\text{MnO}$  up to  $0.4 \text{ mol\%}$ , no significant changes in the position of these bands are observed; however, the tetrahedral band is observed to grow at the expense of the octahedral band. When the concentration of  $\text{MnO}$  is increased beyond  $0.4 \text{ mol\%}$ , both of these  $\text{Mn}^{2+}$  ion bands appear to be masked with the presence of a new absorption band with a peak around  $485 \text{ nm}$ . This band is identified due to  ${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$  transition of  $\text{Mn}^{3+}$  ions

[8]. The summary of data on the positions of various bands in the optical absorption spectra of  $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3\text{: MnO}$  glasses are presented in Table 1.

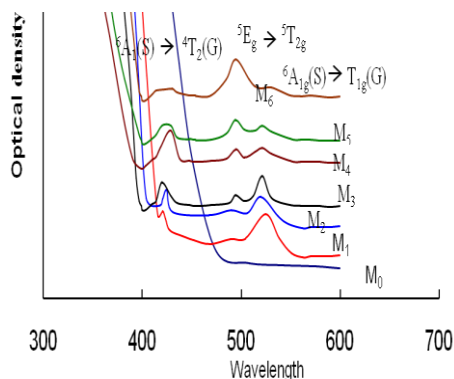


Fig. 1a. Optical absorption spectra of  $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3\text{: MnO}$  glasses

From the observed absorption edges, we have evaluated the optical band gaps ( $E_o$ ) of these glasses by drawing Urbach plot (Fig.1b) between  $(\alpha h\nu)^{1/2}$  and  $h\nu$ . The values of optical band gap ( $E_o$ ) are presented in Table 1. The largest optical band gap is observed for the glass  $M_4$ .

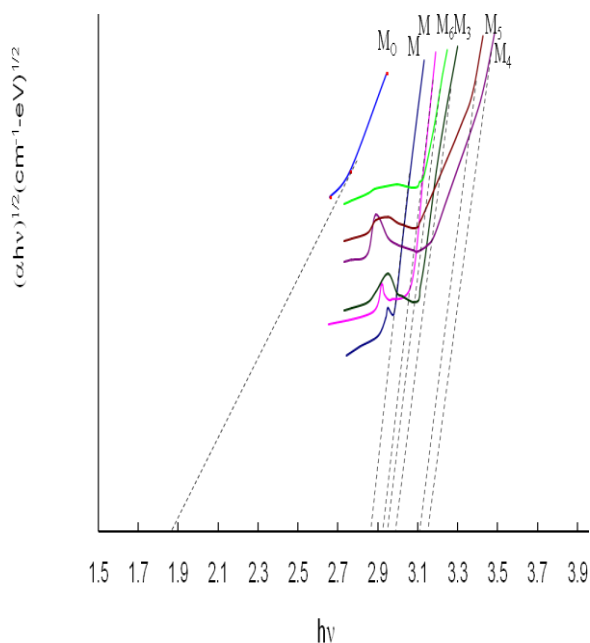


Fig. 1b. Plots to evaluate optical band gaps of  $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3$  glasses containing different concentrations of MnO

Table 1

Summary of data on optical absorption of  $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3\text{: MnO}$  glasses.

Glasses	M	M	M	M	M	M	M
	0	1	2	3	4	5	6
<b>Mn<sup>2+</sup> transitions(nm)</b>							
${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{1g}(\text{G})$	-	520	516	516	-	-	-
${}^6\text{A}_1(\text{S}) \rightarrow {}^4\text{T}_2(\text{G})$	-	-	420	415	424	424	-
<b>Mn<sup>3+</sup> transition (nm)</b>							
${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$	-	-	-	-	490	489	490
<b>Cut-off wavelength (nm)</b>							
	416	392	382	370	346	353	376
<b>Optical band gap (<math>E_o</math> (eV))</b>							
	1.80	2.83	2.89	2.94	3.10	3.06	2.90

Generally, the  $\text{Mn}^{2+}$  complexes exhibit optical absorption bands in the visible and ultraviolet regions. In octahedral symmetry, the ground state of  $\text{Mn}^{2+}$  is spherically non-degenerate  ${}^6\text{A}_{1g}$  state. In a cubic crystalline field of low and moderate strengths, the five d electrons of  $\text{Mn}^{2+}$  are distributed in the  $t_{2g}$  and  $e_g$  orbitals, with three in the former and two in the latter. Therefore, the ground state configuration is normally written as  $(t_{2g})^3(e_g)^2$ . This configuration gives rise to electronic states  ${}^6\text{A}_{1g}$ ,  ${}^4\text{A}_{1g}$ ,  ${}^4\text{E}_g$ ,  ${}^4\text{T}_{1g}$ ,  ${}^4\text{T}_{2g}$ ,  ${}^4\text{A}_{2g}$  and to a number of doublet states of which  ${}^6\text{A}_{1g}$  lies lowest according to Hund's rule. The observed optical absorption bands are from the ground state  ${}^6\text{A}_{1g}$  to some quartet states and these are both spin and parity forbidden. In general,  ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{E}_g(\text{G})$ ,  ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{A}_{1g}(\text{G})$  and  ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{E}_g(\text{D})$  bands are sharp as they arise from intra configurational transitions. The transitions  ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{1g}(\text{G})$  and  ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{2g}(\text{G})$  involve a change of configuration from  $(t_{2g})^3(e_g)^2$  to  $(t_{2g})^4(e_g)^1$  and are therefore observed to be broad [5, 6]. Since all the excited states are spin quartet states, no spin allowed transitions would occur for  $\text{Mn}^{2+}$  ions. Hence,  $\text{Mn}^{2+}$  ions are characterized by weak bands, which arise due to the spin forbidden transitions. By diagonalising the energy matrices for  $d^5$  configuration, the clearly resolved band observed at 520 nm in the optical absorption spectra of  $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3\text{: MnO}$  glasses (containing MnO up to 0.3 mol %) is assigned to  ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{1g}(\text{G})$  transitions and the crystal field parameter  $D_q$  and Racah inter-electronic repulsion parameter B have been determined as  $695\text{ cm}^{-1}$  and  $780\text{ cm}^{-1}$  respectively. The values of the  $D_q$  and B obtained are consistent with the values reported in the literature for number of other glass systems [9-10]. From these values, it may be concluded that in this concentration range divalent manganese ions occupy octahedral positions. Further, the value of B obtained is close to that of free ion value ( $960\text{ cm}^{-1}$ ). Hence, the bonding of manganese ions in the glasses containing low concentration of MnO may be assumed to be ionic in nature. The considerably broad band observed at 415 nm ( $23810\text{ cm}^{-1}$ ) can safely be

ascribed to  ${}^6A_1(s) \rightarrow {}^4T_2(G)$  transition of tetrahedral  $Mn^{2+}$  ions. Further the growth of the band at about 415nm at the cost of band at 515 nm suggests the transformation of  $Mn^{2+}$  ( $d^5$ ) ions from octahedral to tetrahedral environment with increase in the concentrations of MnO up to 0.4 mol %. These tetrahedrally positioned manganese ions occupy network forming positions with  $MnO_4$  structural units and may form linkages with the other network formers. The appearance of a clear broad band in the spectra of the glasses containing MnO beyond 0.4 mol %, at about 485 nm (due to spin allowed  ${}^5E_g \rightarrow {}^5T_{2g}$  transition) indicates that a part of manganese ions exist in  $Mn^{3+}$  ( $d^4$ ) and occupy octahedral positions [8, 10]. Normally, the octahedrally positioned ions (if they do not go in to substitutional positions) act as modifiers. As modifiers, these ions induce bonding defects and non-bridging oxygens by breaking local symmetry and decrease the stability of the glass network. Further, higher the concentration of modifier ions, higher is the concentration of non-bridging oxygens (NBO's) in the glass matrix. This leads to increase in the degree of localization of electrons thereby increasing the donor centers in the glass matrix. The presence of large concentration of these donor centers lowers the optical band gap and shifts the absorption edge towards higher wavelength side as observed when the concentration of MnO is raised beyond 0.4 mol % in the glass matrix.

#### 4.Conclusions

The optical absorption indicates that the presence of manganese ions predominantly in  $Mn^{2+}$  state occupy tetrahedral positions when the concentration of MnO at about 0.4 mol %; whereas beyond 0.4 mol % the manganese ions seem to exist in  $Mn^{3+}$  state.

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